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RESEARCH ON ELECTROCHEMICAL ENERGY  
CONVERSION SYSTEMS

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American University

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The open circuit potentials for the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  are approximately 150 mv closer to the thermodynamic reversible potential than the potential observed in phosphoric acid. On the basis of the electrode kinetic studies of the hydrocarbon electrode and the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  it would be expected that a hydrocarbon-air fuel cell would operate at a substantially higher energy density in this electrolyte as compared with phosphoric acid. Preliminary corrosion tests of four alloys indicate that the  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  electrolyte is substantially less corrosive than phosphoric acid.

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### SUMMARY

The research on electrochemical energy conversion systems has involved work on two tasks: a search for electrolytes alternative to phosphoric acid for direct and indirect hydrocarbon-air fuel cells, and a study of the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells.

The work during this reporting period has dealt with both tasks. The anodic oxidation of propane and the reduction of oxygen (air) were studied in trifluoromethanesulfonic acid monohydrate. Three techniques were used, the galvanostatic pulse technique, the potential ramp technique, and cyclic voltammetry. All three techniques indicate that the enhanced electrode activity of propane in this electrolyte involves a mechanism different from that operating in phosphoric acid and apparently this reaction sequence does not involve certain undesirable intermediates.

The open circuit potentials for the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  are approximately 150 mv closer to the thermodynamic reversible potential than the potential observed in phosphoric acid. On the basis of the electrode kinetic studies of the hydrocarbon electrode and the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  it would be expected that a hydrocarbon-air fuel cell would operate at a substantially higher energy density in this electrolyte as compared with phosphoric acid. Preliminary corrosion tests of four alloys indicate that the  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  electrolyte is substantially less corrosive than phosphoric acid.

#### FOREWORD

This research on electrochemical energy conversion systems has been sponsored by the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir, Virginia under Contract No. DAAK02-72-C-0084 with The American University. The work was authorized under DA Project/Task area/Work Unit No. 1T161102A34A 03 100 EF.

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## 1.0 Introduction

This is the fifth semi-annual report on Contract No. DAAK02-72-C-0084 sponsored by the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir, Virginia. The project entitled "Research on Electrochemical Energy Conversion Systems", consists of two technical tasks, both of which are directed toward the improvement of the hydrocarbon-air fuel cell for ground power systems and vehicular propulsion.

Task I. A search for alternative electrolytes to phosphoric acid for direct and indirect hydrocarbon-air fuel cells.

Task II. A study of the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells.

During this reporting period technical effort was expended on both tasks. The work on Task I involved further investigation of the properties of trifluoromethanesulfonic acid monohydrate as a fuel cell electrolyte, particularly experimentation with the air electrode. In the work under Task II the corrosion rates of four structural alloys were measured in trifluoromethanesulfonic acid monohydrate.

## 2.0 Task I. A Search for Alternative Electrolytes to Phosphoric Acid for Direct and Indirect Hydrocarbon Air Fuel Cells

### 2.1 Introductory

Previous work on this project has indicated that a new electrolyte, trifluoromethanesulfonic acid monohydrate, has certain physical and electrochemical properties which would make it an improved electrolyte over phosphoric acid. The deficiencies of phosphoric acid as a fuel cell electrolyte have been tabulated (1). The search for an "ideal" electrolyte has been guided by a list of properties or characteristics desired of a fuel cell electrolyte.

- a. the electrolyte should be a good medium for the efficient oxidation of the hydrocarbon
- b. the electrolyte should be a good medium for ionic charge transport
- c. the electrolyte should be a good solvent for active materials, e.g. propane, oxygen, water
- d. the electrolyte should be a good medium for material transport, e.g. removal of  $\text{CO}_2$ , as rejection from an acid solution
- e. the electrolyte should be chemically and electrochemically stable over the temperature and voltage operating range of the fuel cell
- f. the electrolyte should possess suitable physical properties, e.g. viscosity and vapor pressure
- g. the electrolyte should not interfere with catalytic reactions, i.e., through anion adsorption or poisoning
- h. the electrolyte should be a good medium for the air electrode, and finally

i. the electrolyte should not be strongly reactive to construction materials or the fuel cell matrix.

At this point it is not possible to express these characteristics in a quantitative manner. For example, it is not possible to assign a critical figure for the hydrocarbon solubility because other mass transport parameters are not known. However, with the above list of properties in mind certain classes of chemical compounds are suggested as possible alternatives to phosphoric acid (1).

a. sulfonic acids, e.g.  $\text{CF}_3\text{SO}_3\text{H}$  (the hydrate concept became apparent as the work progressed).

b. alpha-halo disubstituted carboxylic acids, e.g.  $\text{CHCl}_2\text{COOH}$

c. perfluorocarboxylic acids, e.g.  $\text{C}_2\text{F}_5\text{COOH}$

d. dialkyl phosphate esters, e.g.  $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{OH}$

e. polyphosphates, e.g. Graham's salt

During the last reporting period (2) apparatus was constructed for further investigation of trifluoromethanesulfonic acid monohydrate. This included experimental setups to use a potential ramp technique, to develop cyclic voltammograms, and to measure the solubilities of gases in the electrolyte. Some experiments used a galvanostatic technique to study the anodic oxidation of propane in  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ . Further work investigated the oxidation of propane in perfluorobutyric acid as an example of class c above.

During the present reporting period the results obtained with the potential ramp technique and cyclic voltammetric technique were compared with those obtained with the galvanostatic method, all studying the anodic reaction of propane in  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ . Current density-potential

diagrams for the reduction of oxygen (air) in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  at  $90^\circ$ ,  $115^\circ$ , and  $135^\circ\text{C}$  on smooth platinum were obtained and compared with the reduction of oxygen (air) in 85%  $\text{H}_3\text{PO}_4$ . In the continuing study of the physical properties of the electrolyte the solubility of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  was determined at  $90^\circ$ ,  $104^\circ$ , and  $126^\circ\text{C}$ .

## 2.2 Experimental

### 2.2.1 Preparation of Electrolytes

#### Trifluoromethanesulfonic acid monohydrate

Trifluoromethanesulfonic acid monohydrate was prepared from the trifluoromethanesulfonic acid (3 M Corporation, Fluorochemical Acid FC-24, Lot 17) and water by the method of Gramstad and Haszeldine (3). This method which involves successive distillations produced the acid monohydrate as a white, needle-like crystalline product with a sharp melting point at  $34^\circ\text{C}$  in agreement with the above referenced work. This preparation is described in more detail under Task II (section 3.2).

#### Phosphoric acid (85%)

Phosphoric acid (Fisher, 85% ACS Grade) was further purified by the technique previously described (4). In this technique the commercial acid is treated with 30%  $\text{H}_2\text{O}_2$ , concentrated, rediluted to 85% acid, and finally pre-electrolyzed. This 85%  $\text{H}_3\text{PO}_4$  was used as a comparison electrolyte to evaluate results obtained with the  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  electrolyte.

### 2.2.2 Apparatus and Techniques

#### Electrochemical Studies

The electrochemical cell and reference system have been described in an earlier progress report (1). The cell was a standard three-compartment cell of approximately 30 ml capacity to conserve the volume of the expensive

electrolyte required per experiment. The technique used to electrochemically clean the electrolyte before the electrooxidation or electroreduction, as well as the method used to determine the surface area of the electrode were similar to those described in the referenced progress report.

Helium, propane, and air were used in different experiments. Helium (AIRCO) was passed over hot copper turnings to remove traces of oxygen before being passed into the cell. Propane (Matheson "Instrument" Grade) and Air (Air Products, "Breathing Quality") were used without pretreatment. All gas lines, which were Teflon tubing, were heated so that the gases as they entered the cell were close to the operating temperature of the cell. The cell itself was maintained at temperature in an air oven.

When phosphoric acid was used as the electrolyte it was necessary to humidify the gases before they were passed into the electrochemical cell. This was accomplished with a two compartment pyrex humidifier maintained at a temperature of 55° to replace the water lost by the phosphoric acid (initially 85%) in the cell.

The electroreduction of air was studied in both electrolytes. Current-potential measurements were made for the reaction in 85%  $\text{H}_3\text{PO}_4$  and  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  at 95°, 115°, and 135°C. The electronic apparatus has been described previously (4). In making these current-potential measurements the practice was to set the potential and then allow the system to equilibrate for five minutes before reading the value of the current. Current-potential measurements were found to reach a steady state more rapidly if the cell was run with air overnight under a potential of approximately 0.90 v. vs the dynamic hydrogen electrode. (All potentials

given in this report are with reference to the dynamic hydrogen electrode). In constructing the potential-current curve it was customary to use a patterned sequence for the potentials. This patterned sequence used a constant potential difference, e.g., a typical sequence was 0.95, 1.25, 0.90, 1.20, 0.85, 1.15, 0.80, 1.05, 0.75, 1.00 volts. This method was used instead of the customary sequence of 0.75, 0.80, 0.85, 0.90, 0.95, 1.00, etc. The use of the patterned sequence produced reproducible voltage-current diagrams after a shorter number of runs than did the normal 50 mv potential step procedure. After two or three runs the patterned sequence resulted in reproducible potential-current diagrams whereas the 50 mv step technique might take as many as four to five runs to develop reproducible potential-current diagrams. This essentially duplicates the procedure used successfully by Walker (5).

In the study of the propane adsorption process in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  two multipulse potentiodynamic methods were used. The electrical block diagram and technique were described in the last interim progress report (2). The pulse sequence is given in figure 1. In the first instance, figure 1a, a potential ramp was imposed on the electrode following a series of pretreatment steps. In the second instance, figure 1b, a potential triangle was imposed following the pretreatment steps. In these techniques, the electrode is pretreated to develop a reproducible surface, an adsorption step is conducted at the potential of interest, and finally a potential wave form (ramp or triangle) is imposed on the electrode.

### Solubility Studies

The gas solubility apparatus and procedure were described in some detail in the last progress report (2). This procedure is essentially that reported by Loprest (6) but modified to use a precision pressure gauge (Texas Instrument, Model No. 145-02). The procedure involves introducing a measured quantity of gas into the system containing a known volume of solvent (in this case  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ ) and measuring the equilibrium pressure of the system. During this last reporting period the solubility of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  at several temperatures was measured.

### 2.3 Results

#### Electrochemical reduction of air in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ Current-potential diagrams

In the development of the hydrocarbon-air fuel cell the performance of the air electrode is obviously as important as the hydrocarbon side. For that reason an investigation of the current-potential behavior of the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  was conducted. These data were compared with data obtained for the reduction of air in 85%  $\text{H}_3\text{PO}_4$ . The results on the electroreduction of air in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  on platinum mesh at 95°, 115°, and 135°C are summarized in figure 2. The results have been "normalized" for surface area and adjusted to the "average" open circuit potential. In "normalizing" for surface area the observed current value for the electrode reaction was divided by the "real" surface area of the electrode as determined by the cathodic galvanostatic charge associated with the deposition of hydrogen atoms on a clean electrode prior to  $\text{H}_2$  evolution.

The "average" of the open circuit potentials was the average of the open circuit potentials observed for several current-potential runs

at each temperature. The deviation from this average for each run was approximately 20 mv.

The current density values at a set potential increase with temperature as would be expected. The observed limiting current densities were

135 $\mu\text{a}/\text{cm}^2$	at	95°C
170 $\mu\text{a}/\text{cm}^2$	at	115°C
190 $\mu\text{a}/\text{cm}^2$	at	135°C

It was observed during the course of running the current-potential curves that the open circuit potential increased during the first few runs toward the reversible thermodynamic oxygen potential. Following the first few runs the open circuit potential became stable during the remainder of the experiments. This effect is observed in the runs reported in figure 3.

Figures 4, 5, and 6 compare the results for the reduction of air in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  with those for 85%  $\text{H}_3\text{PO}_4$  at 95°, 115°, and 135°C. At all temperatures the current carrying ability at any given potential is higher in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ . The limiting current density is also higher in this electrolyte than in 85%  $\text{H}_3\text{PO}_4$  although the dramatic enhancement observed for the propane reaction is not evident in the air reaction. The most significant feature of these plots is the higher open circuit potential (approximately 150 mv higher) for the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  as compared with the open circuit potential in 85%  $\text{H}_3\text{PO}_4$ .

The open circuit potential for air in 85%  $\text{H}_3\text{PO}_4$  reported here is approximately the same as that reported in the literature (7). The open circuit potential in inorganic acids which is considerably lower than the thermodynamically calculated value, is usually regarded as a mixed potential.



Figure 1a:

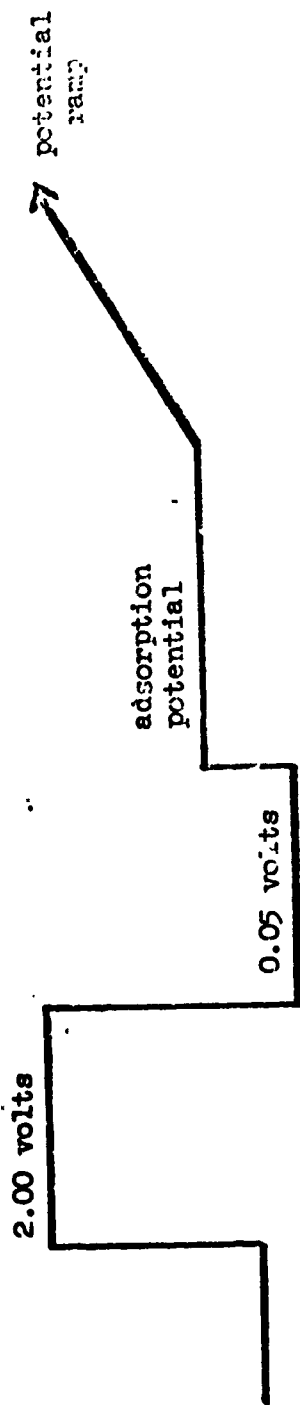


Figure 1b

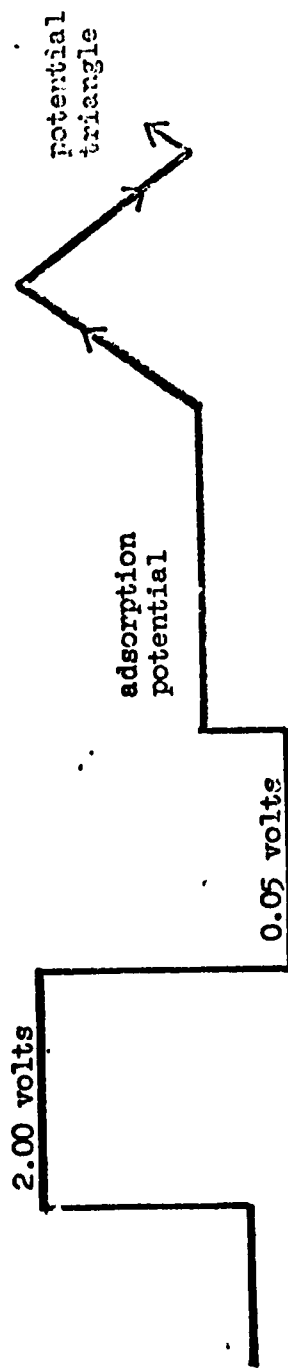


Figure 1. Pulse sequences used to study propane adsorption;

1a potential ramp following pretreatment;

1b potential triangle following pretreatment

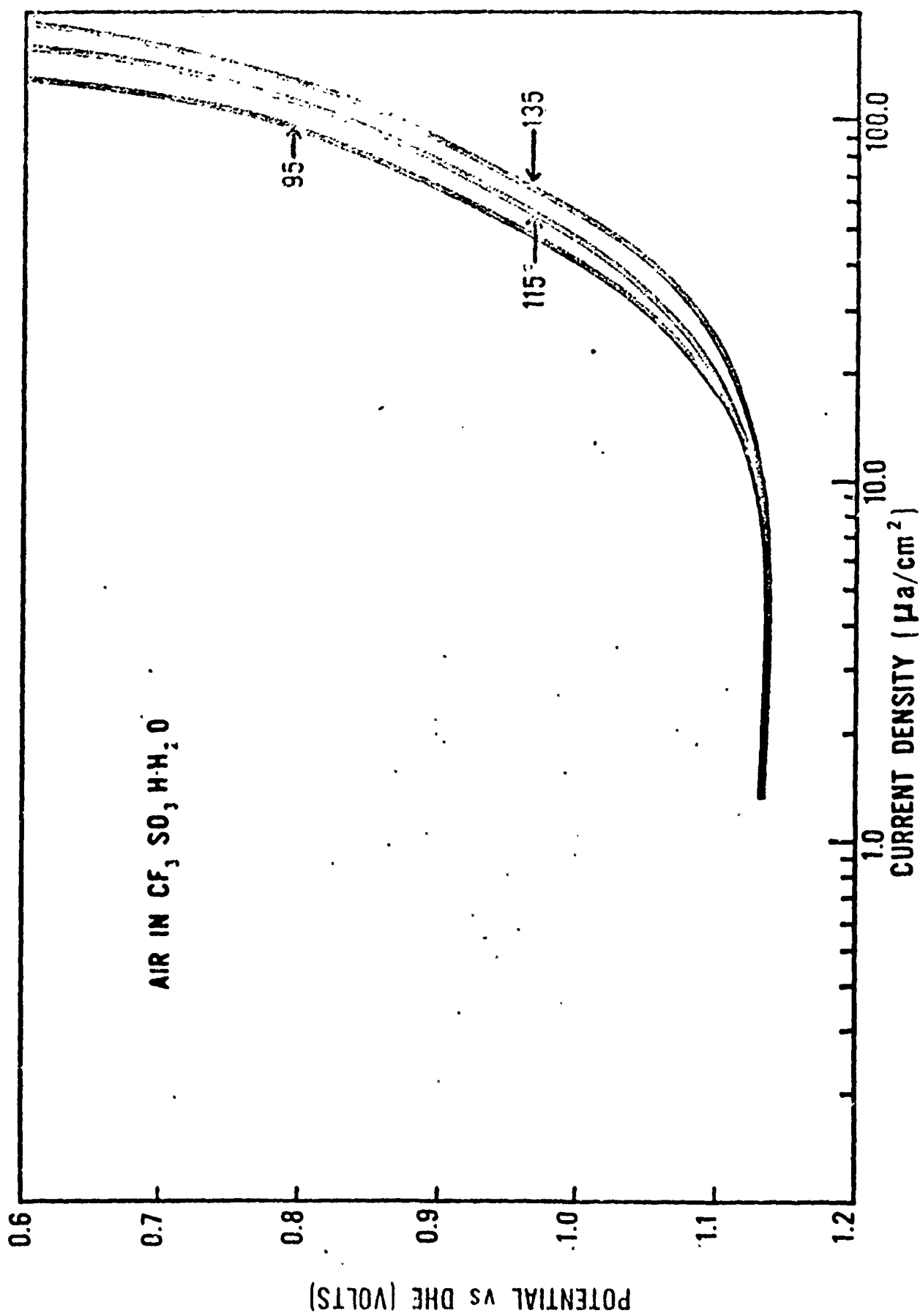


Figure 2. Electroreduction of air in  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  at 95°, 115°, and 135°C.

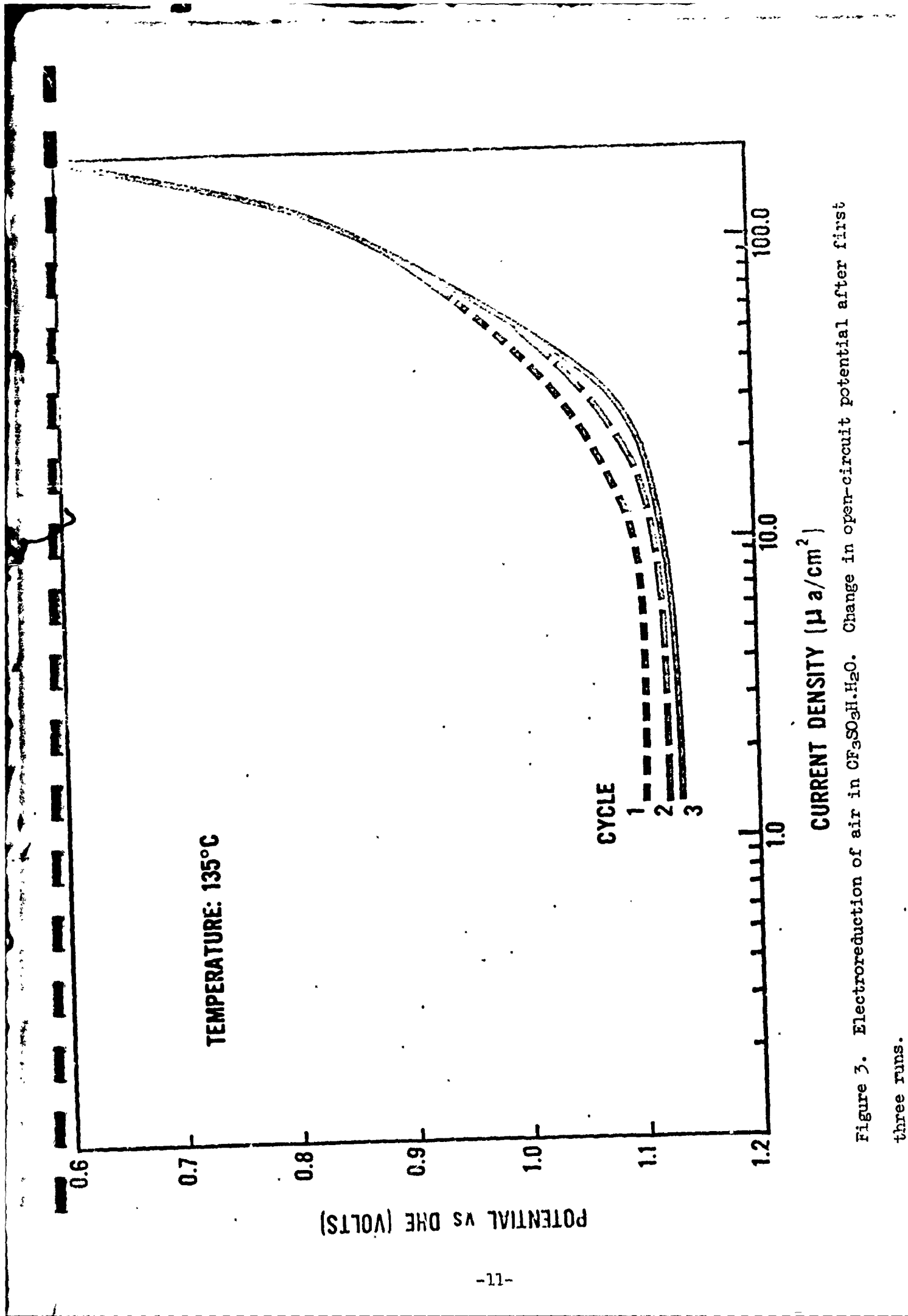


Figure 3. Electroreduction of air in  $CF_3SO_3H.H_2O$ . Change in open-circuit potential after first three runs.

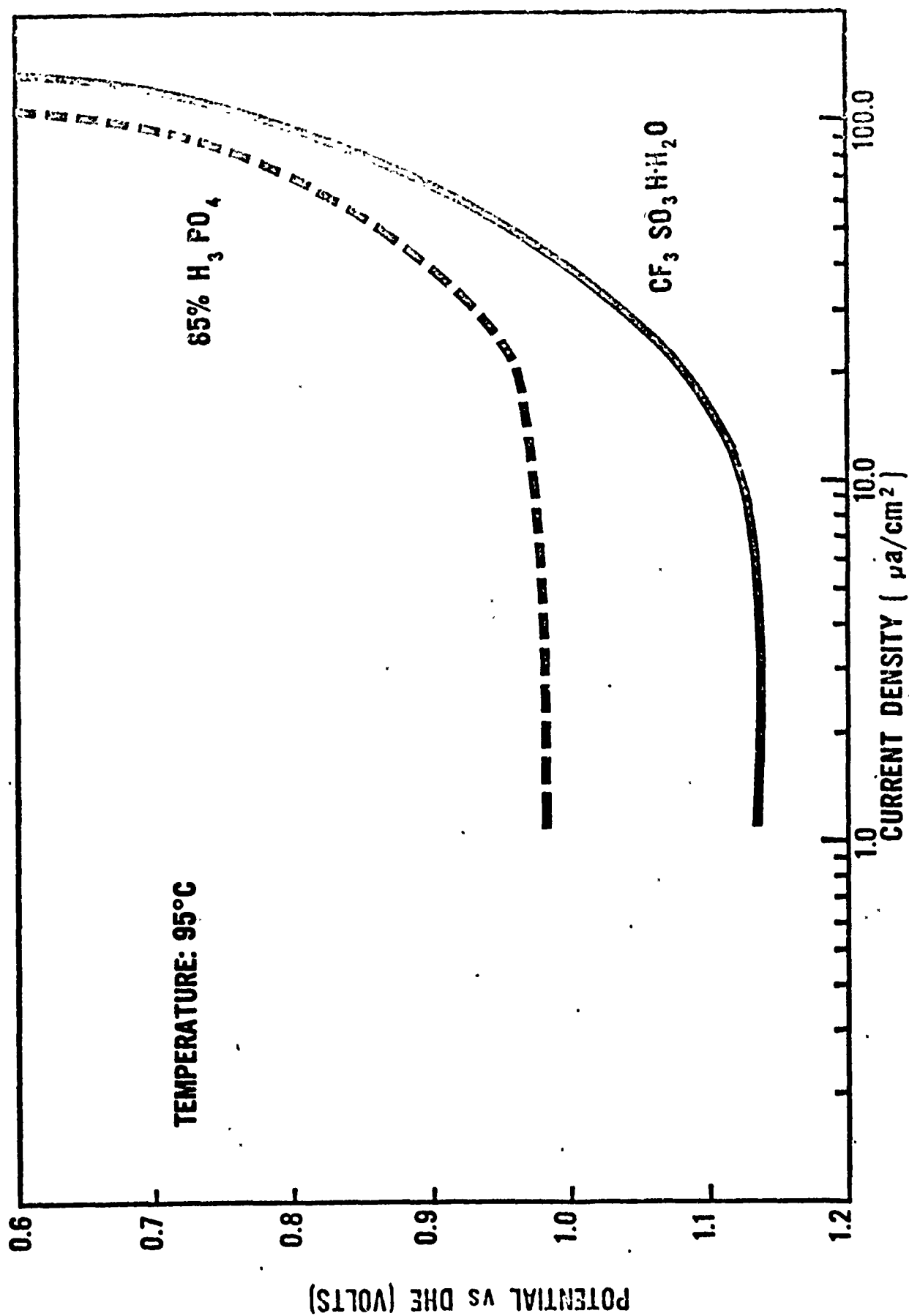


Figure 4. Electroreduction of air in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  compared with reaction in  $\text{H}_3\text{PO}_4$ . Temperature 95°C.

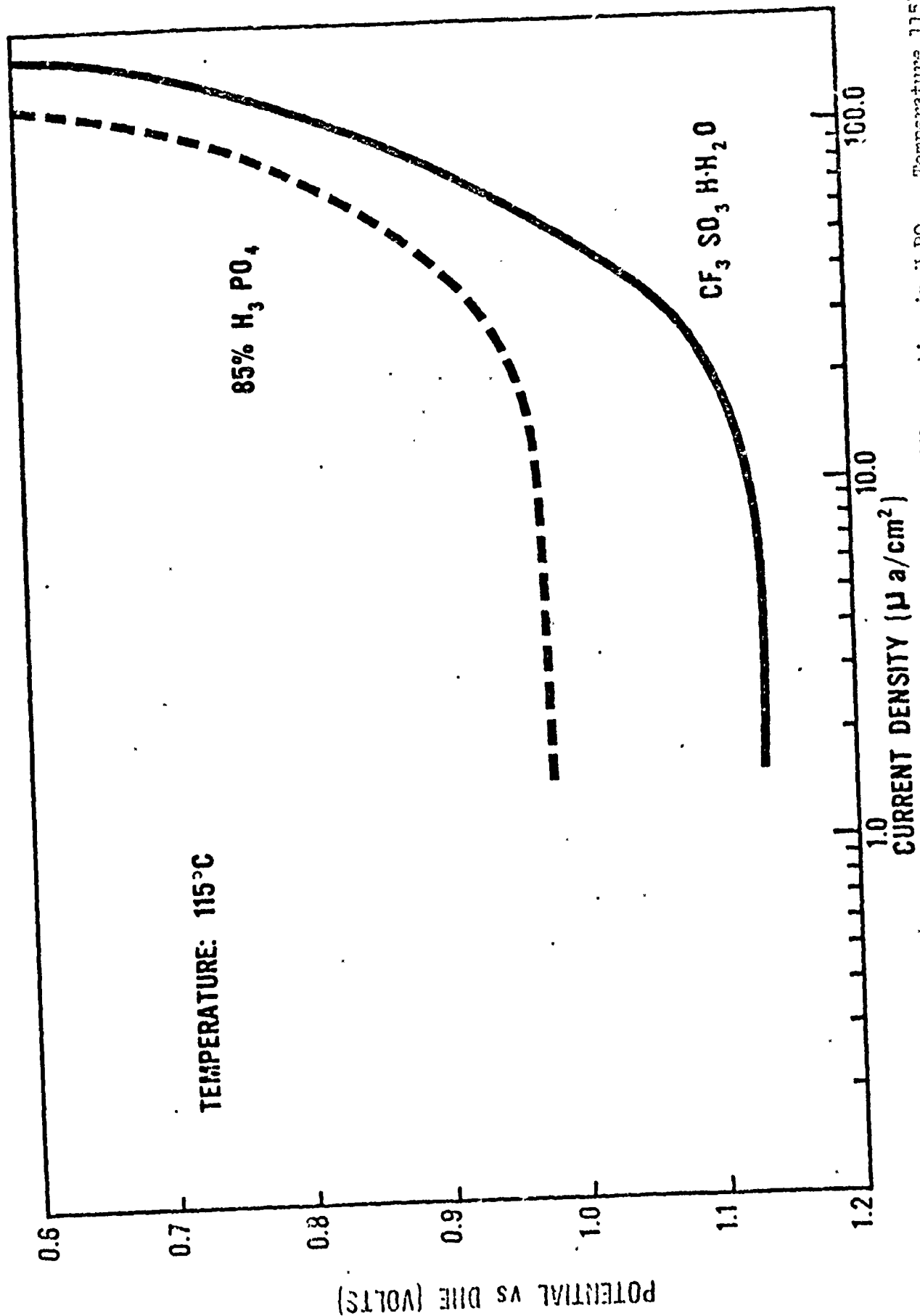


Figure 5. Electroreduction of air in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  compared with reaction in  $\text{H}_3\text{PO}_4$ . Temperature 115°C.

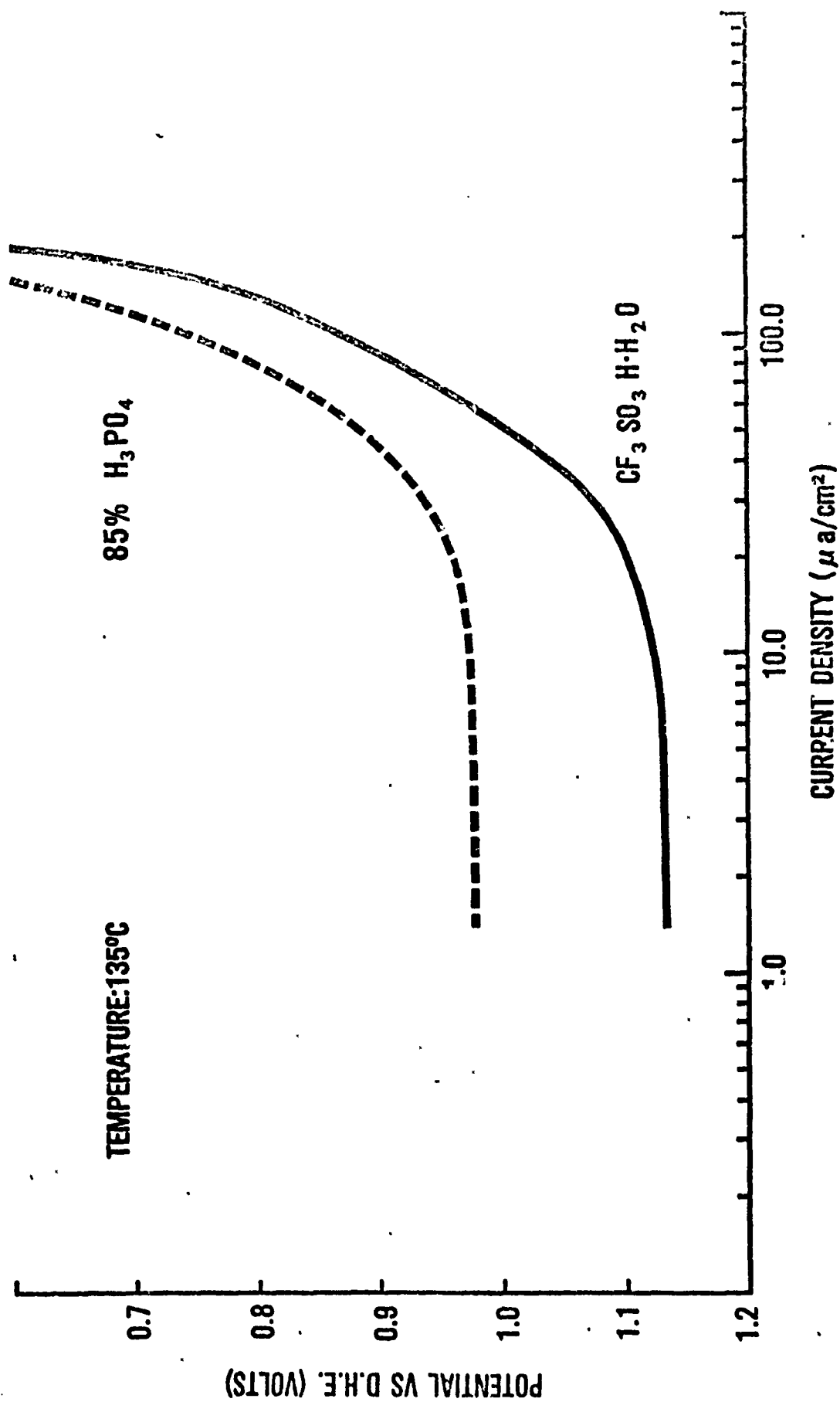


Figure 6. Electroreduction of air in  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  compared with reaction in  $\text{H}_3\text{PO}_4$ . Temperature 135°C.

Several models have been put forth to explain the difference between the thermodynamically calculated value and the observed mixed potential. These include the formation of peroxides during the oxygen reaction in acidic solution (8); the existence of Pt/PtO and PtO/PtO<sub>2</sub> couples (9); and a potential established by impurities, particularly organic impurities (10).

At the present time it would be a matter of speculation in attempting to explain the higher potential for the air electrode in CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O.

The exchange current density calculated for the air electrode in CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O is approximately 10<sup>-8</sup> amp/cm<sup>2</sup>. Literature values for the air electrode in 85% H<sub>3</sub>PO<sub>4</sub> fall in the range of 10<sup>-10</sup> to 10<sup>-7</sup> amp/cm<sup>2</sup>, the reported values depending considerably on impurities in solution and other factors. The "Tafel" slope calculated from the polarization curves in CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O was 0.62 which is close to the value obtained from similar experiments in phosphoric acid.

In figure 7 the experimental observations on the air electrode and the propane electrode, in the two electrolytes, H<sub>3</sub>PO<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O, both at 135°C, are brought together. It is clear that a higher potential difference is developed in the CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O electrolyte. For example, at a current density of 1.0 μamp/cm<sup>2</sup> potential differences exist of

0.84 volt in CF<sub>3</sub>SO<sub>3</sub>H·H<sub>2</sub>O

0.67 volt in 85% H<sub>3</sub>PO<sub>4</sub>

or a difference of 170 mv. Correspondingly, at 4.0 μamp/cm<sup>2</sup> a 210 mv. potential difference exists.

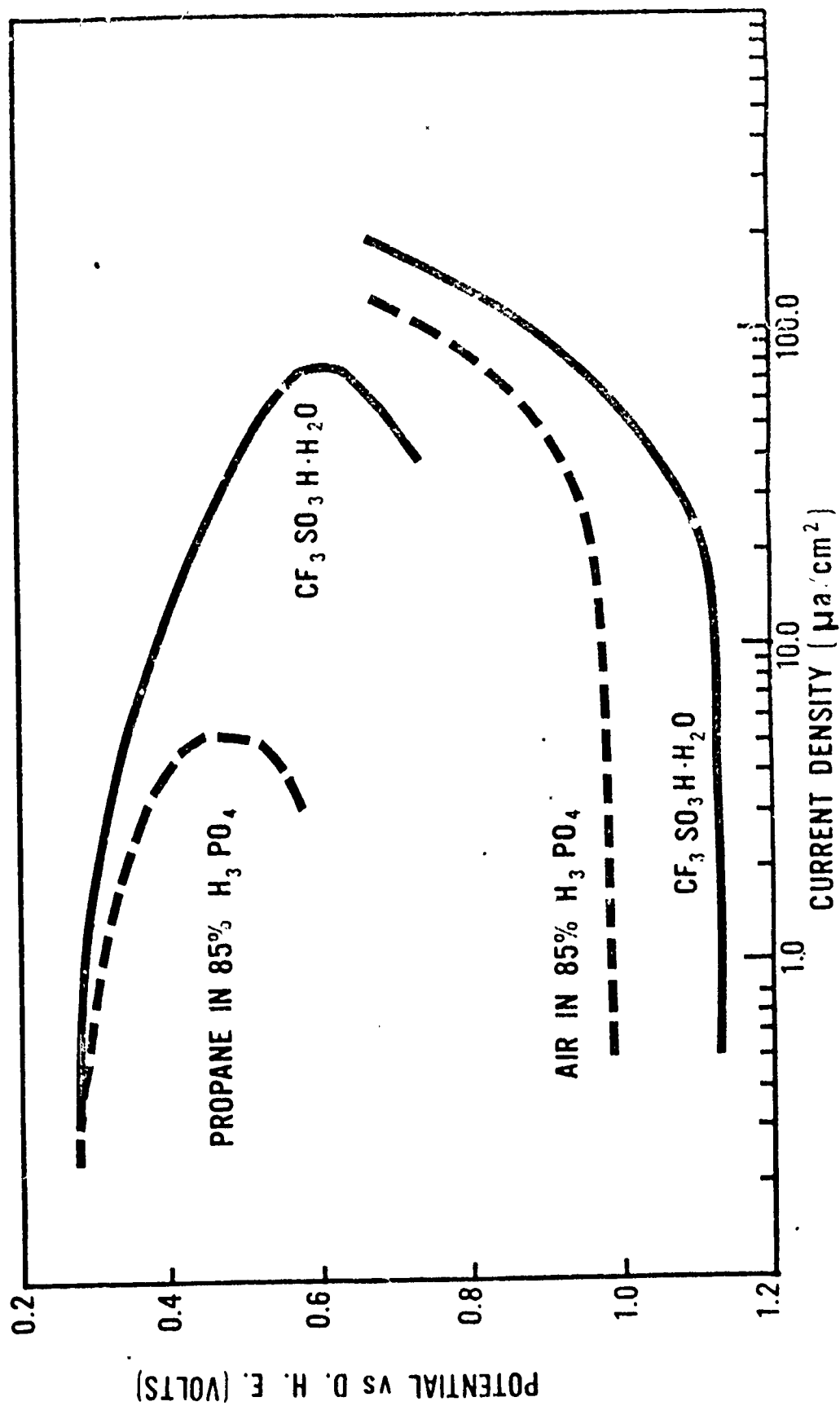


Figure 7. Current potential diagrams for propane and air compared for the two electrolytes,  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$ .



### Electrochemical behavior of propane in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ - Potential

#### Ramp Technique

Measurements utilizing the potential ramp technique, begun during the last reporting period, were continued during this period. The measurements were extended to include a wider adsorption range, 0.20 to 0.60 volts, and adsorption times varying from 2 to 10 minutes. Typical curves for propane oxidation in the two comparison electrolytes are given in figure 8. At all adsorption potentials and at all adsorption times a single oxidation peak was observed for the oxidation of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ . In 75%  $\text{H}_3\text{PO}_4$  two oxidation peaks are clearly distinguishable (11). These results corroborate the results observed using the galvanostatic pulse technique (2).

#### Electrochemical behavior of propane in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ - Cyclic Voltammograms

A limited number of cyclic voltammograms were run to support the observations made with other techniques regarding the anodic oxidation of propane. A typical cyclic voltammogram is shown in figure 9. This voltammogram was run after a 5 minute adsorption of propane at an adsorption potential of 0.30 volts. The single oxidation peak is observed at approximately 0.8 volts.

The three techniques, galvanostatic pulse, potential ramp, and cyclic voltammetry support the conclusion of the existence of a different reaction mechanism for the anodic oxidation of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  as contrasted to that in  $\text{H}_3\text{PO}_4$ .

PROPANE IN 75%  $\text{H}_3\text{PO}_4$

PROPANE IN  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

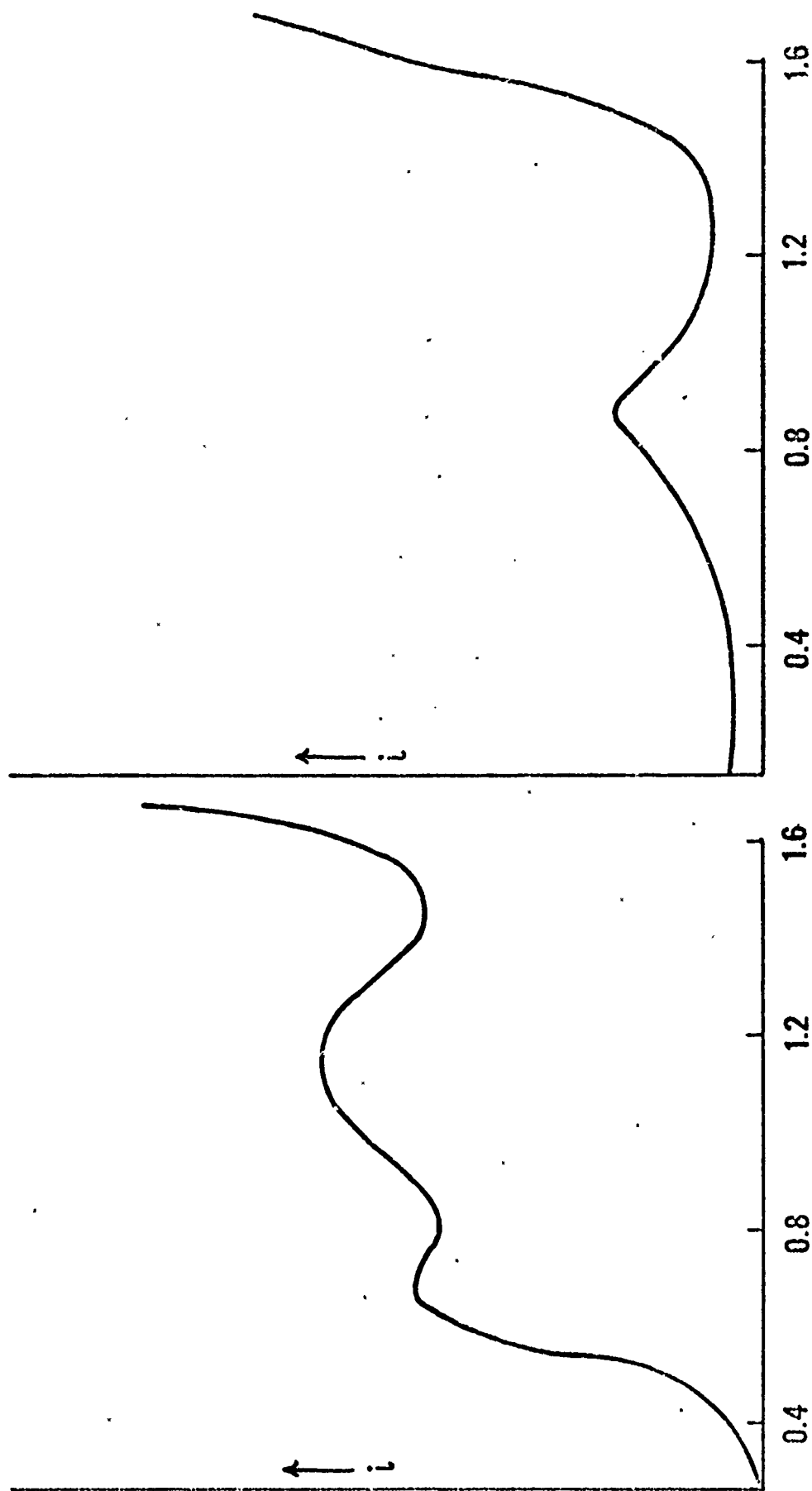


Figure 8. Anodic oxidation of propane in 75%  $\text{H}_3\text{PO}_4$  and in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  - Potential Ramp Technique

# PROPANE IN $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

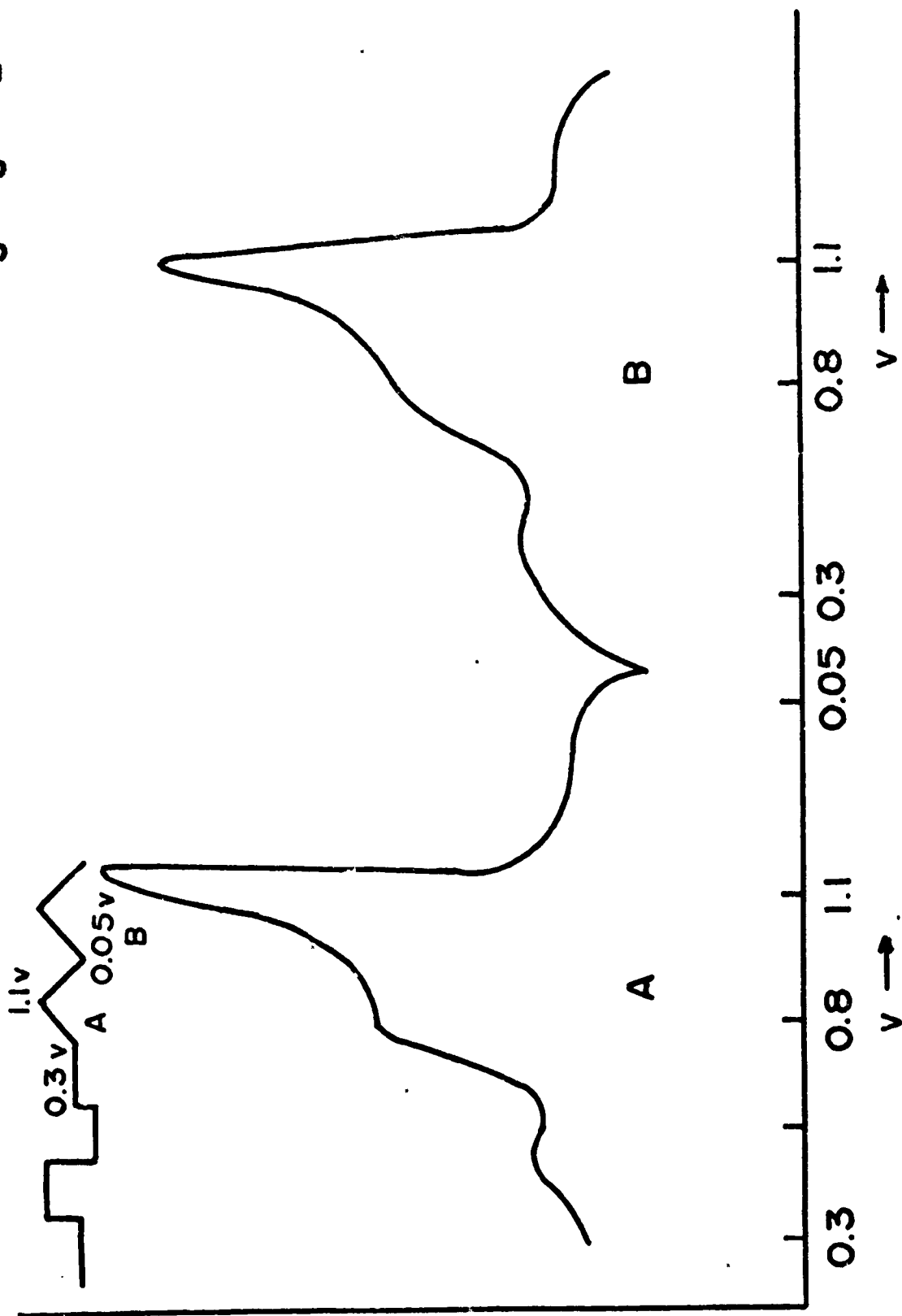


Figure 9. Anodic oxidation of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  - Cyclic Voltammogram.

### Solubility Measurements

In the last progress report (2) the check of the gas solubility apparatus using the solubility of oxygen in water was reported. The apparatus and technique were considered to be sufficiently accurate to proceed to measurement of gas solubilities in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ . The solubility of propane was determined at  $90^\circ$ ,  $104^\circ$ , and  $126^\circ\text{C}$ . With the existing apparatus it was not possible to work over  $126^\circ\text{C}$  because during the degassing procedure for the solvent some of the  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  charge in the solvent bulb was carried over and condensed in the other portions of the apparatus. It was not possible to accurately determine the volume of solvent lost from bulb but this volume was available to absorb the gas when the propane was introduced.

The solubility of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  at three temperatures is as follows:

<u>Temperature</u>	<u>Solubility (millimoles of propane/liter <math>\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}</math>)</u>	<u>Pressure of propane</u>
$90^\circ\text{C}$	0.127	770 mm.
$104^\circ\text{C}$	0.102	780 mm.
$126^\circ\text{C}$	0.35	770 mm.

The  $126^\circ\text{C}$  value is considered less reliable than the other two for the reasons given above. The values in the above table may be compared with a literature value for the solubility of propane in concentrated  $\text{H}_3\text{PO}_4$ . MacDonald reports(12) a value of 0.153 millimoles of propane per liter of 93%  $\text{H}_3\text{PO}_4$  at  $100^\circ\text{C}$  and 754 mm of propane.

## 2.4 Conclusions

The work during the last reporting period has contributed to our knowledge of both the hydrocarbon electrode and the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ . From this and the preceding work, it appears definite that a direct hydrocarbon-air fuel cell utilizing this electrolyte would support a considerably higher energy density than the corresponding cell utilizing phosphoric acid.

The anodic oxidation of propane has been studied with three techniques, the galvanostatic pulse technique, the potential ramp technique, and cyclic voltammetry. The results of all three techniques indicate that the mechanism operating in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  differs from that operating in  $\text{H}_3\text{PO}_4$ . It is suggested that at least one of the detrimental intermediates observed in the phosphoric acid mechanism is absent in the  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  mechanism. The solubility determinations do not indicate any appreciable differences in the two electrolytes. There is no evidence at this point to conclude that the reason for the enhanced electrode activity of propane in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  lies in improved mass transport.

The open circuit potentials for the air electrode in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  were approximately 150 mv. closer to the thermodynamic reversible oxygen potential than the potential observed in phosphoric acid. It is speculated that the reason for this is related to the interference with the peroxide reaction.

### 3.0 Task II A Study of the Corrosion Characteristics of Electrolytes for Intermediate-Temperature Hydrocarbon-Air Fuel Cells

#### 3.1 Introductory

The objective of this task was to make corrosion measurements on selected alloys that might be used as construction materials in a fuel cell with a  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  electrolyte. The first selection of materials was made from those alloys that are known to be relatively resistant to corrosion in solutions of strong acids.

#### 3.2 Experimental

The alloys and their approximate compositions are given in Table I. These alloys are commercially available. Prior to testing, the alloy samples were pre-treated according to the following procedure. They were cleaned in acetone to remove grease from the surface. After drying in air the samples were immersed in  $\text{HCl}$  (1:1) at  $85^\circ$  for 1-2 minutes. Following this they were rinsed in distilled water and then dipped in a solution of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (1:1). They were again rinsed in distilled water, rinsed with acetone, and stored in dry acetone until they were used for the corrosion test. At that time they were removed and allowed to dry in the air before being weighed.

The monohydrate of trifluoromethanesulfonic acid was prepared by the method referred to above (section 2.2.1). In this preparation the acid (Trifluoromethanesulfonic acid, FC-24, Lot 017, from the 3M Co.) was mixed with  $\text{H}_2\text{O}$  (60 ml. of acid with 12 ml  $\text{H}_2\text{O}$ ). This mixture was distilled with the fraction under  $150^\circ\text{C}$  being rejected. A second distillation was made by holding at about  $150^\circ\text{C}$  until no more distillate came off. The solution temperature was then raised and the distillation

Table I Composition of Alloys Used in Corrosion Tests

<u>Alloy</u>	<u>Composition</u>
AISI Type 304	18.0-20.0 Cr; 8.00-11.0 Ni; 0.03 C (max); 2.0 Mn (max); 1.00 Si(max); 0.045 P (max); 0.03 S (max); balance Fe
Incoloy 825	42 Ni; 21 Cr; 3.0 Mo; 33 Fe
Hastelloy C	56 Ni; 15 Cr; 3.7 W; 16 Mo; balance Fe
Carpenter 20 Cb-3	34.03 Ni; 19.91 Cr; 2.25 Mo; 3.30 Cu; 0.21 Co; 0.86 Cb; 0.039 C; 0.39 Mn; 0.41 Si; 0.016 P; 0.004 S; balance Fe

continued at 213-215°C. The latter distillate was collected. The final distillation was made with approximately a 600 ml volume. The first 50 ml. were rejected and 500 ml boiling at 217-218°C (756.9 mm) was collected. The compound, so prepared, supercooled to about 25°C before crystallizing and melted sharply at 33°C. This boiling point of 217-218°C is higher than that previously reported (1) and much of the difference has been found to be due to an inaccurate thermometer used in the previously reported preparation. With this new, more accurate, boiling point and the literature values for vapor pressure of 1 mm at 96° (3) and 15 mm at 120° (13) it is possible to construct an improved vapor pressure curve (figure 10). It is recognized that this curve must still be considered rather rough but it does offer the possibility of making an estimation of the vapor pressure of the hydrate at working fuel cell temperatures. Thus, from the plot, vapor pressures of

31 mm at 135°C

64 mm at 150°

185 mm at 175°

may be read. This explains why no difficulty has been encountered in making electrochemical studies at 135°C.

Immediately following distillation, 20 ml aliquots of the hydrate were transferred to test tubes fitted with Teflon stoppers. After the alloy samples were weighed they were immersed in the  $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$  which had been equilibrated in the constant temperature oil bath for about one hour. The corrosion tests were run in duplicate for a duration of 4 hours at 110°C and 161°C. Following the exposure, the samples were rinsed successively with distilled water and acetone, dried and reweighed.



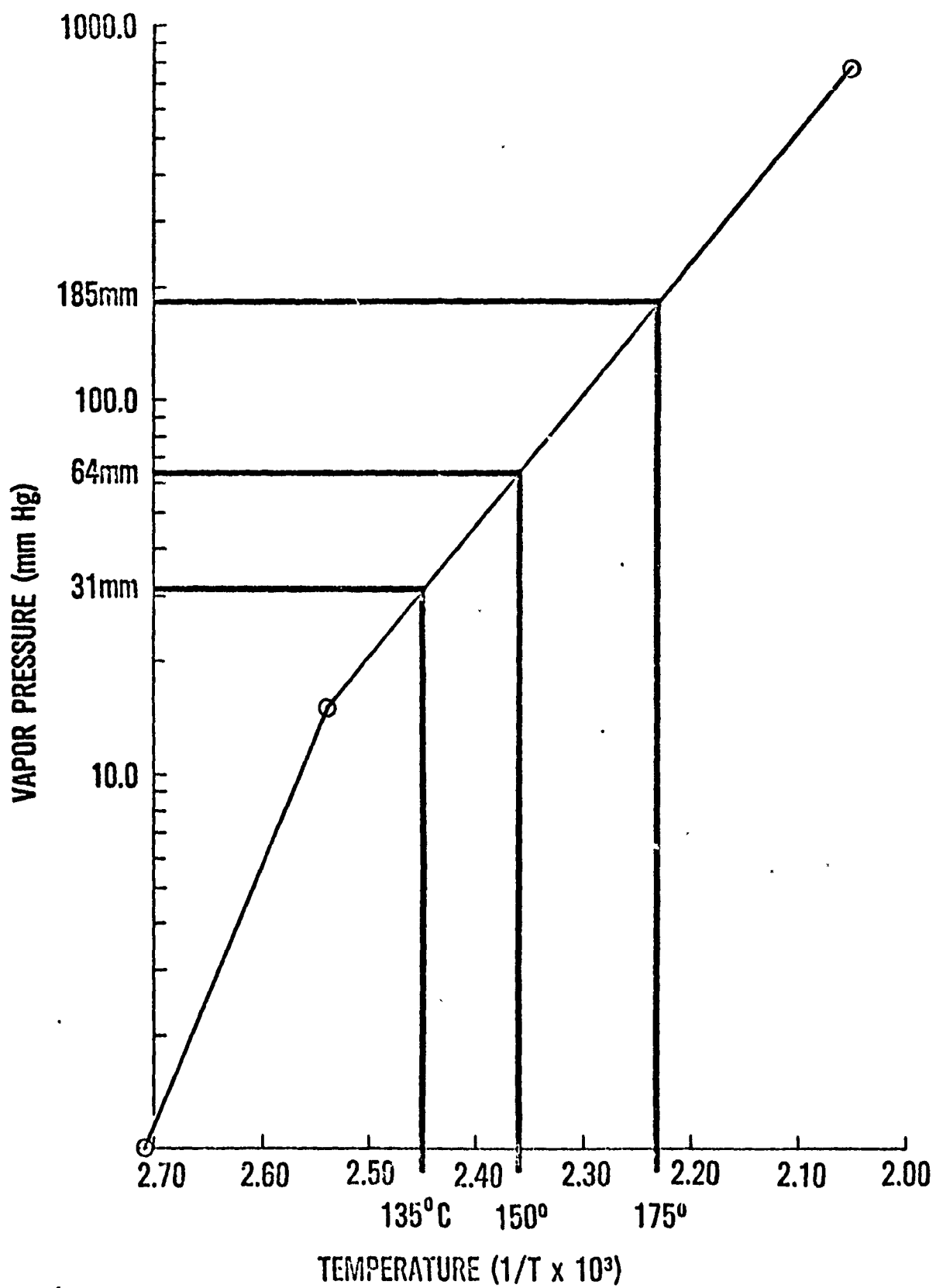


Figure 10. Vapor pressure - temperature curve for trifluoromethanesulfonic acid monohydrate.

### 3.3 Results

The corrosion data are given as weight losses in Table II. These weight losses are good measures of the corrosion of the alloys in the sense that the coupons did not develop corrosion product films, the weight of which would be included in the weight of the sample after exposure to the acid. Further, there was no evidence for the formation of high resistivity surface films. It is apparent that the corrosion rates for all four alloys are quite low at 161°C. The 4 hr rate of  $0.3 \text{ mg cm}^{-2}$  for stainless steel type 304 compares with a 4 hr rate of  $40 \text{ mg cm}^{-2}$  observed in phosphoric acid (4). A corrosion rate of  $0.3 \text{ mg cm}^{-2}$  may be converted to an engineering corrosion rate unit of 0.036 inches penetration per year, a rate that usually can be tolerated in construction materials for tanks, piping, and valves.

### 3.4 Conclusions

On the basis of these preliminary results it would appear that it will not be necessary to use the highly alloyed Ni or Cr steels to contain the acid. Stainless steel AISI type 304 or Ni-plate steel should provide adequate corrosion resistance to serve as a construction material. Rather the problem is shifted to an electrochemical question dealing with the concentration (in trace quantities) of  $\text{Fe}^{++}$ ,  $\text{Ni}^{++}$ , etc. than can be tolerated in the electrolyte. In this preliminary study the metals reacted at their corrosion potential. The probability exists that a different rate, greater or lesser, would exist if the metal was held at a positive or negative potential, e.g., as a current collector.

#### 4.0 Future Work

In pursuit of the investigation of the two tasks set down in the Introduction it is intended to perform the following specific studies during the next reporting period.

a) Further electrochemical studies, such as cyclic voltammometric studies, will be performed on the reduction of air in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ .

These will include the determination of the effect of flow rate on the limiting current density of the cathodic reaction.

b) The solubility of oxygen in  $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  will be determined at several temperatures.

c) The anodic oxidation of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO-H}_2$  mixtures will be investigated.

d) In the extended future it would be desirable to investigate higher homologs of the fluorinate sulfonic acids either individually or as additives to trifluoromethanesulfonic acid monohydrate. This could include tetrafluoroethanedisulfonic acid studied by Camp and Baker (14).

Table II. Corrosion of Alloys in Trifluoromethanesulfonic acid monohydrate

Alloy	Loss at weight ( $\text{mg cm}^{-2}$ ) in 4 hours	
	<u>At 110°C</u>	<u>At 161°C</u>
AISI type 304 (Stainless steel)	0.21 Ave. 0.14 0.07	0.28 Ave. 0.31 0.33
Incoloy 825	0.026 Ave. 0.03 0.026	0.22 Ave. 0.28 0.33
Hastelloy C	0.06 Ave. 0.06 0.06	0.37 Ave. 0.37 0.36
Carpenter 20-Cb3	0.14 Ave. 0.11 0.09	0.31 Ave. 0.31 0.29

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